

US EPA ARCHIVE DOCUMENT

Shaughnessy No: 034805

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TO: Frank Rubis
Product Manager #50
Registration Division (H7505C)

FROM: Emil Regelman, Supervisory Chemist
Environmental Chemistry Review Section #2
Environmental Fate and Ground Water Branch, EFED (H7507C)

THRU: Henry M. Jacoby, Chief
Environmental Fate and Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of:

Reg./File #: 034805

Common Name: "Ziram"

Zinc Dimethyldithiocarbamate; Bis(dimethylcarbamo-
Chemical Name: dithioato-S,S')zinc; Bis(dimethyldithiocarbamato)zinc

Type product: Fungicide

Carbazinc; Corozate; Cuman; Drupina 90; Fungostop; Hexazir;
Product Name: Mezene; Prodaram; Tricarbamix Z; Tricabol; Vanicide; Zerlate;
Zincamate; Ziramvis; Zirasan 90; Zirberk; Zirex 90, Ziride

Company Name: Ziram Task Force

Purpose: Review of environmental fate data submitted in response of
ground water Data Call-In for ground-water leaching assessment

Date Received: a) 2/5/87; b) 2/11/88 a) 87-0864
EFGWB #: b) 88-0418

Action Code: a) 495; b) 400 Total Reviewing Time (decimal days): 4.0

Deferrals to: _____ Ecological Effects Branch, EFED
_____ Science Integration & Policy Staff, EFED
_____ Non-Dietary Exposure Branch, HED
_____ Dietary Exposure Branch, HED
_____ Toxicology Branch I , HED
_____ Toxicology Branch II, HED

1. CHEMICAL:

Common Name: Ziram

Chemical Name(s): Bis(dimethyldithiocarbamato)zinc
Bis(dimethylcarbamodithioato-S,S')zinc
Zinc bis(dimethyldithiocarbamate)

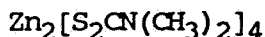
CAS #: 137-30-4

Trade name(s):

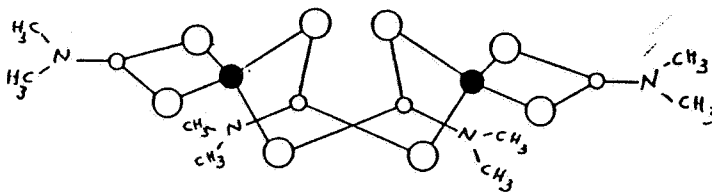
Carbazinc, Corozate, Cuman, Drupina 90, Fungostop, Hexazir, Mezene, Proraram, Tricarbamix Z, Tricabol, Vanicide, Zerlate, Zincmate, Ziramvis, Zirasan 90, Zirberk, Zirex 90, Ziride, Zitox.

Structure:

" $\text{Zn}[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$ " is actually a binuclear molecule, which should be represented as



The molecular structure of this compound was determined by Klug (Klug, H.P. 1966. "The crystal structure of zinc dimethyldithiocarbamate", Acta Cryst., Vol.21, pp. 536-546) and it is represented below,



Idealized structure of the $\text{Zn}(\text{Me}_2\text{Dtc})_2$ complex. (O) S, (●) Zn, (o) C.

(Taken from D. Coucouvanis, "The Chemistry of Dithioacid and 1,1-Dithiolate Complexes", in Progress in Inorganic Chemistry, John Wiley and Sons, New York, 1970, Volume 11. pp. 233-371)

The coordination of sulfur about each Zn atom is distorted tetrahedral. Two of the four dimethyldithiocarbamato ligands act as bridging groups between the two zinc atoms; the other two ligands are chelated directly to the zinc atoms. The average Zn-S distance is 2.362 Å.

Physical/Chemical properties:

Molecular formula: $\text{Zn}_2[\text{S}_2\text{CN}(\text{CH}_3)_2]_4$

Molecular weight: 611.6 (based on the determined molecular structure)

Physical state: Colorless powder; Melting Point: 240°C

Vapor pressure: "Negligible" at room temperature (ca. 10^{-7} Torr)

Solubility (25°C):

Water.....65 mg/L
Slightly soluble in,
 diethyl ether
 ethanol
Moderately soluble in acetone
Soluble in,
 dilute alkali
 carbon disulfide
 chloroform

2. STUDY/ACTION TYPE:

Review of environmental fate studies for ground water assessment.

3. STUDY IDENTIFICATION:

Accession No. 260071

- Carpenter, M. 1985a. Determination of photodegradation of ziram in aqueous solution. ABC Final Report #33398. Unpublished study prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO. Submitted by the Ziram Task Force through Prochimie International, New York, NY.

Accession No. 260071

- Carpenter, M. 1985b. Determination of photodegradation of ziram on the surface of soil. ABC Report #33370. Unpublished study prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO. Submitted by the Ziram Task Force through Prochimie International, New York, NY.

MRID #40061601

- Cranor, W. 1987a. Aerobic soil metabolism study with ¹⁴C-ziram. ABC Final Report #33366. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Columbia, MO. Submitted by Penrwalt Corporation, Philadelphia, PA.

MRID #40061602

- Cranor, W. 1987b. Anaerobic soil metabolism study with ¹⁴C-ziram. ABC Final Report #33367. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Columbia, MO. Submitted by Penrwalt Corporation, Philadelphia, PA.

MRID #40497301

- Daly, D. and Cranor, W. 1987. Determination of hydrolysis rate with ¹⁴C-ziram. ABC Final Report #33363. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Columbia, MO. Submitted by the Ziram Task Force through Penrwalt Corporation, Bryan, TX.

Accession No. 258213

- Lemal, R., Boel, C., and Debondues, M. 1984. Ziram: Rate of hydrolysis as a function of pH. Note L.P.C.D. No. 130-84. Unpublished study prepared by Drogenboes Laboratory, B-Drogenboes, Belgium. Submitted by the Ziram Task Force through Prochimie International, New York, NY.

Accession No. 258212

- Lemal, R. and Debondues, M. 1984. Ziram: Determination of octanol/water partition coefficient. Unpublished study prepared by UCB-Drogenbos Laboratory, B-Drogenbos, Belgium. Submitted by the Ziram Task Force through Prochimie International, New York, NY.

MRID #40061603

- Selman, F. 1987a. Ziram soil dissipation study. ABC Preliminary Report #35028. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO and Morse Laboratories, Inc., Sacramento, CA. Submitted by Pennwalt Corporation, Philadelphia, PA.

MRID #40061604

- Selman, F. 1987b. Ziram soil dissipation study. ABC Preliminary Report #35029. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO and Morse Laboratories, Inc., Sacramento, CA. Submitted by Pennwalt Corporation, Philadelphia, PA.

7 Accession No. 259584

- Warren, J. 1985a. Determination of adsorption/desorption constants of [¹⁴C]-ziram. ABC Report #33368. Unpublished report prepared by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO. Submitted by the Ziram Task Force through Prochimie International, Inc., New York, NY.

Accession No. 259584

- Warren, J. 1985b. Leaching characteristics of aged ziram. ABC Report #33364. Unpublished report prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO. Submitted by the Ziram Task Force through Prochimie International, Inc., New York, NY.

Accession No. 259584

- Warren, J. and Connor, S. 1985. Leaching characteristics of parent ziram. ABC Report #33365. Unpublished study prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO. Submitted by the Ziram Task Force through Prochimie International, Inc., New York, NY.

4. REVIEWED BY:

Silvia C. Termes, Chemist
Review Section #2
EFGWB/EFED/OPP

Signature: 

Date: March 9, 1990

5. APPROVED BY:

Emil Regelman
Supervisory Chemist
Review Section #2
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Signature: 

Date: MAR 15 1990

6. CONCLUSIONS:

None of the reviewed studies were considered acceptable and, therefore, cannot be used to fulfill Subdivision N Guidelines for ziram. In addition, the questionable results obtained from these studies precludes an accurate ground-water leaching assessment for ziram.

The main problems encountered with the studies are mostly related to their experimental design and analytical methodology. In some studies it is reported that ziram and its degradates are unstable and cannot be extracted from soil or water nondestructible; in other studies, however, it is reported that these degradates were extracted (but were neither identified nor quantified).

Although carbon disulfide (CS_2) is an expected decomposition product of dithiocarbamate ligands, trapping of CS_2 was ineffective. One of the best methods to trap CS_2 is by using an aliphatic alcohol/strong alkali solution trap. The reaction between the alkoxide (RO^-) and the electrophile CS_2 produces an alkyl dithiocarbonate (xanthate), which can be subsequently quantified by spectrophotometric methods (characteristic absorption band at 301 nm; molar absorptivity of the order of $10^3 \text{ l mole}^{-1} \text{ cm}^{-1}$), electrochemical techniques, or chromatographic methods. Very recently ion chromatography has been applied to the analysis of xanthates and degradation products (see Palsson, B.I. "Analysis of xanthate and its degradation products by ion chromatography", Trans. Inst. Min. Met., Section C 98 (1989), pp. C132-C140); similar technique may be applicable to the analysis of alkyl dithiocarbamates. Another alternative method of "trapping" evolved CS_2 involves the use of benzyl mercaptan and potassium hydroxide in 80% ter-butyl alcohol to form the bright yellow potassium benzyl trithiocarbonate, which has a chromophore at 430 nm (molar absorptivity $2.10 \times 10^2 \text{ l mole}^{-1} \text{ cm}^{-1}$; this method is believed to produce better results than the xanthate method (Verma et al., Talanta, vol.30 (1983), pp.787-788).

Therefore, because of the contradictory information provided about the adequacy of analytical methods for ziram and its degradates, the registrant needs to provide the EFGWB with a discussion of the analytical methods currently available for use with ziram, detailing the advantages and limitations of each. It should be kept in mind that with the availability of more sophisticated chemical instrumentation, analytical methods (particularly confirmatory methods) could be improved and, in many instances, in-situ measurements during the course of the study may be feasible. (for example, use of diode-array UV-VIS spectrophotometers with continuous flow-through; electrochemical techniques; Fourier-Transform Infrared "FT-IR" Spectrometry; ion chromatography, etc.).

A summary of the chemistry of dithiocarbamate/zinc compounds and related species is presented in the APPENDIX. This summary is based on published chemical literature information. Structures of parent ziram and possible degradation products are also shown in the APPENDIX.

Summary of the Environmental Fate Behavior of Ziram

Although the data reviewed was unacceptable to fulfill Subdivision N Guidelines or to do a comprehensive environmental fate/leaching potential assessment of ziram, the following general observations can be made:

- a. The hydrolysis behavior of ziram appears to be consistent with that of the free dialkyldithiocarbamate ligands. That is, decomposition became faster with decreasing pH. However, reaction products were not identified.
- b. The experimental design/conditions of the photodegradation studies was not adequate and precludes the use of results to assess the effect of "sunlight" radiation on ziram in aqueous solutions and on soils. It was observed that volatilization from irradiated samples was greater than from nonirradiated samples.
- c. From the aerobic soil metabolism study there is evidence that ziram residues were present at ca. 12% of the applied radioactivity after one year of treatment. However, the residues were not characterized and it is not known if they are associated with parent ziram or with other species. Volatiles (unidentified) reached a total high of ca. 84% of the applied radioactivity after one year. This suggests that dissipation by formation of volatile species may be an important dissipation pathway for ziram. Under anaerobic conditions, ziram appears to be persistent, but the results are of limited value.
- d. Column leaching studies (unaged) suggest that ziram residues (nature unidentified) are mobile in sandy and sandy loam soils. Aged residues also appear to be mobile. None of the residues (in soil or in leachates) were characterized.
- e. From terrestrial field dissipation studies there is some evidence that ziram residues do not tend to accumulate after repeated treatments. There is also some evidence that ziram residues moved to the 12-inch depth. The nature of the residues (parent and/or degradates) is not known because residues were determined as total CS₂. Another major problem encountered with these studies was the poor storage stability of the samples, which was not taken into account in the design of the actual field dissipation studies.
- f. The low octanol/water partition coefficient of parent ziram (ca. 12) suggests that parent ziram will have a low tendency to accumulate in fatty tissues. It should be pointed out, however, that if the more hydrophobic "thiuram disulfide" degradate forms, then there is the potential for this degradate to accumulate in fatty tissues.

Thus, from the very incomplete data base available at this time it appears that a major mode of dissipation for ziram may be through formation of volatile degradates and that nonvolatile ziram residues show mobility in soils. However, the lack of adequate analytical methodology to identify these residues does not allow to make any conclusions as to which of the species (parent or degradates) are mobile.

7. RECOMMENDATIONS:

The registrant should be informed of that none of the studies submitted are acceptable to fulfill environmental fate data requirements. Therefore new studies are required.

As explained in the CONCLUSIONS Section, the main problems with these studies appear to be related to the experimental design and the adequacy of the analytical methodology. The registrant needs to provide an updated discussion of the analytical methods currently available for the identification/characterization of ziram and its degradates. Attention should be paid to the feasibility of using in-situ measurements during the course of a study (see CONCLUSIONS Section).

For the new studies, submission of detailed protocols is highly recommended.

For the terrestrial field dissipation studies, the registrant should refer to the recently released Standard Evaluation Procedure (SEP) for Terrestrial Field Dissipation studies (EPA-540-09/90-073; December 1989) when designing their studies. The registrant may also wish to consider the use of steel cylinders driven into the soil, which will allow the use of radiolabeled parent material. If cylinders are used, It is recommended that provisions be made to effectively trap volatile degradation products (this will not be necessary for all of the cylinders placed in the field, but only on selected cylinders).

EFGWB also recommends that characterization of the test material by X-ray diffraction be considered (that is, by comparing the X-ray diffraction powder pattern of the test material with published crystallographic data).

Copies of the Data Evaluation Records (DERs) should be made available to the registrant for detailed comments to each of the individual studies.

9. BACKGROUND:

a. Introduction

The data reviewed here was received as the result of a Ground-Water Data Call-In for this chemical issued on 7/20/84 and was submitted by the Ziram Task Force, which included Pennwalt Corporation, UCB Chemicals, R.T. Vanderbilt, Yucan Inc., Montedison Group, and FMC Corporation.

b. Directions for Use

Ziram is a protective fungicide registered for use on terrestrial food crop (orchard, vineyard, and field and vegetable crops), greenhouse food crop, and terrestrial nonfood crop (ornamentals) sites.

c. Status of Environmental Fate Data Requirements

None of the data requirements for any of the above-listed use patterns have been satisfied.

9. DISCUSSION OF INDIVIDUAL STUDIES:

See Data Evaluation Records for each of the reviewed studies.

10. CBI APPENDIX:

No CBI.

APPENDIX

Summary of Chemical Properties of Bis(dimethylcarbamodithioato-S,S')zinc based on Published Chemical Literature

As noted on page 1, the molecular structure determination of this compound showed that the compound is actually a binuclear molecule in which the two zinc atoms are bridged by two dimethyldithiocarbamato ligands and with the two other remaining ligands chelated to each of the Zn atoms. Thus, the correct molecular formula for ziram should be expressed as $\text{Zn}_2[\text{S}_2\text{CN}(\text{CH}_3)_2]_4$.

The following reaction pathways should be considered in the degradation of the parent molecule: a) breakage of the Zn-S bond; b) reactions the free ligand; and c) reactions of the "free" Zn^{2+} .

It is known that noncoordinated alkyl/dialkyl dithiocarbamato ligands are in aqueous media are prone to decomposition to CS_2 and the parent amine and that the decomposition becomes faster with decreasing pH. Oxidation reactions are also known, in which the oxidation product is the disulfide (tetraalkylthiuram disulfide). The oxidation with I_2 is well-known and the reaction with Cu(II) salts to produce the Cu(I)-dithiocarbamato complex and the "thiuram disulfide" is also known*. The "thiuram disulfides" are more hydrophobic species than the free ligand. The disulfide may loose one of the sulfurs in the disulfide bridge to yield the "thiuram monosulfide"

If "free Zn^{2+} " (that is, Zn(II) not coordinated to any of the dialkyldithiocarbamato ligands) is formed, the distribution of Zn(II) species in aqueous solution will be determined by the pH of the medium.

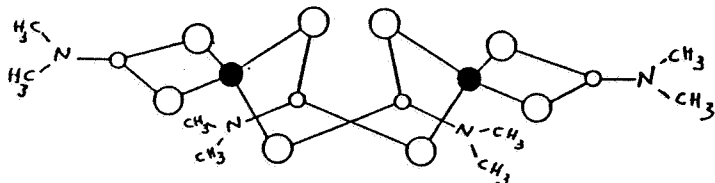
The reaction of the "bis(dimethyldithiocarbamato)zinc" to produce "thiuram disulfide" has been reported. Also the reaction of the parent compound with a free ligand is known to produce the tris ionic complex $[\text{Zn}(\text{Me}_2\text{CN}(\text{CH}_3)_2)_3]^-$; the structure of this compound, as the tetraethylammonium salt, has been determined (Chem. Comm., 1976, p.743).

It should also be kept in mind that CS_2 can undergo reaction to carbonyl sulfide (COS); this reaction is known to occur in the presence on hydroxyl radicals. In soils under aerobic conditions CS_2 can undergo reaction to sulfate and carbonate.

References:

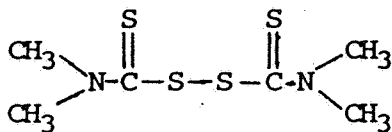
- Coucouvanis, D. Progress in Inorganic Chemistry, v.11, pp.233-371, (1970), John Wiley and Sons, New York
- Coucouvanis, D. Progress in Inorganic Chemistry, v.26, pp.301-469, (1979) John Wiley and Sons, New York
- Burns, R.P., McCullough, F.P., and McAuliffe, C.A. Advances in Inorganic and Radiochemistry, v.23, pp. 211-280, (1980), Academic Press, New York.
- Eisenberg, R. Progress in Inorganic Chemistry, v.12, pp. 295-369 (1970), John Wiley and Sons, New York.
- Cotton, F.A. and Wilkinson, G. Advanced Inorganic Chemistry, Fifth Edition, 1988, John Wiley and Sons.
- Atkinson, R. Chem. Rev., v.85. pp.69-201, (1985).

* These reactions have been used in some analytical methods for the determination of CS_2 via formation of an alkyl dithiocarbamate.

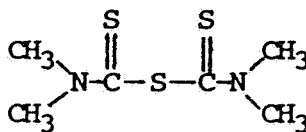


Idealized structure of the $\text{Zn}(\text{Me}_2\text{Dtc})_2$ complex. (○) S, (●) Zn, (○) C.

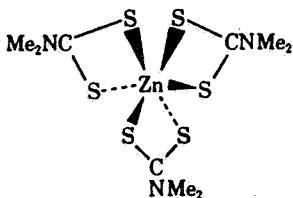
"ZIRAM"
("Zinc dimethyldithiocarbamate")



"Tetramethylthiuram disulfide"
("TMDD; ENT"; "Thiram")
Tetramethylthioperoxydicarbonic diamide;



Tetramethylthiuram monosulfide
("TMIM")



Tris(dimethyldithiocarbamato)zinc(II) anion

Other possible degradates derived from the decomposition of a "free" dithiocarbamate ligand: CS_2 , dimethylamine. Carbon disulfide can further react to form carbonyl sulfide (COS). Microbial degradation could lead to formation of mercaptans.

Zn(II) species in aqueous media (distribution is pH-dependent):
" Zn^{2+} ", ZnOH^+ , $\text{Zn}(\text{OH})_2$ (solid), HZnO_2^- , ZnO_2^{2-}